

Control of metal impurities in “dirty” multicrystalline silicon for solar cells

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Abstract

The rapid growth of the global photovoltaics (PV) industry is increasingly limited by the availability of suitable Si feedstock material. Therefore, it is very important to explore new approaches that might allow processing of solar cells with satisfactory energy conversion efficiency based on inexpensive feedstock material with less stringent impurity control, i.e., “dirty” silicon. Our detailed studies of the distribution of metal impurity clusters in multicrystalline Si have demonstrated that cells with the same total impurity content can have widely different minority carrier diffusion lengths based on the distribution of the metals, i.e., whether they are dispersed throughout the material or concentrated in a few, large clusters. Possible approaches to defect engineering of metal clusters in silicon are discussed.

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The problem of availability and specifications for silicon feedstock suitable for solar cell fabrication has been a cause of concern since solar cells became a commercial product. Silicon accounts for approximately 25–50% or more (depending on the technology and the type of silicon used) of the cost of processed solar cells, which has a major impact on the competitiveness of photovoltaics (PV) in the energy market. The fluctuations of availability and feedstock cost determine the profitability of photovoltaic manufacturers, their production volume, and expansion plans. The explosive growth of the solar cell industry has already driven up the price of electronic grade silicon, and an immediate solution to the feedstock supply crunch is not yet clear. According to P. Maycock’s PV News newsletter, in 2005 the worldwide PV industry grew 44% and reached an estimated 1.7 GW_p of installed capacity. At this growth rate, it will not be long before the silicon demand for solar cells surpasses that of the whole integrated circuits industry.

The cost of raw silicon is determined by its purity. While metallurgical grade (MG-Si) silicon costs not more than US\$ 1–1.50 kg^{−1}, semiconductor grade polysilicon can cost any-

where from US\$ 35 to 200 depending on the market conditions. If the photovoltaic industry could use “dirty” silicon with less stringent specifications for purity than electronic grade silicon, a substantial gain in cost and availability could be realized. As early as 1982, Bathey and Cretella [1] pointed out in their review that the cost of silicon could be reduced by a factor of 10 by reducing the purity requirements from <1 ppb (semiconductor grade silicon) to 0.5–100 ppm. Feedstock supplies for the PV industry that have intermediate impurity constraints have been dubbed solar-grade silicon (SoG-Si), although there is not as yet a consensus concerning what the ultimate specifications should be.

SoG-Si can be manufactured either by simplification or modifications [2–6] of the standard Siemens process based on distillation of silicon-rich gaseous compounds, or by purification of metallurgical grade silicon to reduce concentrations of P, B, Al, O, C, and transition metals. In general, SoG-Si routes utilize significantly less energy than the standard Siemens process, thus reducing both costs and energy payback times. The purification processes that are most frequently mentioned in the literature include one of the following technologies or their combination.

- (a) *Reduction of silica by carbon:* This process uses the same reaction that is used for manufacturing metallurgical-grade silicon in an arc furnace ($\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$). The typical impurity level in MG-Si manufactured through this

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process is 98–99% and even 95% because the raw materials used in this process contain high impurity levels. It is possible to obtain much higher degree of purity of silicon at a reasonable cost by using either naturally clean, or purified by leaching silica or quartz and carbon black or pelletized activated carbon with higher than average purity in specially designed arc furnaces with purified electrodes [2,7–14].

- (b) *Acid leaching*: This approach calls for pulverizing MG-Si in powder with 70 μm or less particle size, and then treating this powder with various acids (e.g., aqua regia, hydrochloric acid, hydrofluoric acid) to dissolve metal clusters, which are frequently found in MG-Si at grain boundaries and are exposed during powdering [1]. It is possible to obtain silicon with the purity of 99.9–99.97% [15–17]. The disadvantage of this process is that it is not effective in removing impurities dissolved intragranularly in high concentrations, e.g., B and P.
- (c) *Gas blowing through the silicon melt*: A purity level of 99.99% can be achieved by blowing gases such as Cl_2 , O_2 , SiCl_4 , wet hydrogen, CO_2 , or their combinations [18,19]. These gases react with impurities dissolved in silicon and form volatile compounds which evaporate from the melt. For example, chlorides of many metals and BOH are volatile. This method is effective in removing, e.g., Al, Ca, C, Mg, Fe, B, P, and Ti.
- (d) *Directional solidification*: During crystal pulling from the melt (e.g., Czochralski or float zone growth) or directional solidification of the molten silicon (e.g., float zone Si, ingot-grown mc-Si) impurities segregate in the melt [2,14,20]. At the end of the growth run, the majority of impurities is found in a thin layer near the top of the directionally solidified ingot or remains in the crucible. Such purification runs can be used to improve the purity of mc-Si. The efficiency of removal of impurities from silicon depends on their segregation coefficients. In general, metals segregate much more effectively than shallow dopants.
- (e) *Melting and refining of silicon with a reactive plasma*: A plasma torch is used to melt the near-surface layer of silicon and to activate gases such as argon, hydrogen, oxygen, and water vapors. These gases react with impurities in the melt and form volatile compounds [21–28]. Both metals and dopants can be removed.
- (f) *Evaporation of phosphorus from the surface of the silicon melt*, heated to boiling temperatures in the near-surface area of a crucible by an electron beam in vacuum [29,30].
- (g) *“Slagging” or calcium leaching*: These approaches are based on mixing silicon with a chemical that has high affinity to undesirable impurities, binds them in a stable compound, and can later be separated from the silicon through deposition on the crucible walls, filtering through the mesh, or acid and solvent leaching. For instance, addition of Ca was successfully used for reduction of Fe, Ti, and P concentrations [31]. Another example is immersion of crushed silicon in a metal with low melting point, such as aluminum, silver, or zinc [32]. Silicon may be completely liquefied by forming a Si–Al eutectic at temperatures well below the melting point of Si (such as 1100 °C). During cooling, the solubility

of Si in Al decreases and silicon precipitates are formed, which are separated from the molten Al by filtering through a mesh. Si pellets are cleaned from Al by acid leaching.

The list above, which is by no means complete, shows that technologies for inexpensive and energy-efficient purification of silicon are readily available. One of the chief obstacles on the road to their wide-scale commercialization is the lack of understanding in the photovoltaic community of what contamination levels are acceptable. To make things more complicated, the critical contamination levels are likely to differ among sheet, ribbon, and directional ingot solidification technologies, and may be affected by small changes in the growth and solar cell processing conditions.

It is instructive to compare typical impurity concentrations in MG-Si, SoG-Si, and standard mc-Si currently used for solar cells. The plot presented in Fig. 1 is based on the data from Refs. [1,3,23,33–38]. There is no legend in Fig. 1 because the link between the sets of bars in the plot and data sources is not important. We are concerned about the general trends. One can see that the impurity content in MG-Si (top graph in Fig. 1) is very high, but the values from different sources rarely vary by more than an order of magnitude. The impurity content in commercial mc-Si (the bottom graph in Fig. 1) is two to five orders of magnitude lower than in MG-Si, and some elements such as Ti, Mn, V, Zr, Mn, are below the detection limit of neutron activation analysis. The variation in metal concentration by one to two orders of magnitude reflects the differences in growth conditions and in the quality of feedstock used by different manufacturers. Finally, the most interesting in this figure is the metal concentration in SoG-Si (the middle graph in Fig. 1). These data are based on analyses of materials which went through one or several steps of purification of MG-Si. Two facts are worth noting. First, there is huge (up to three orders of magnitude) variation in reported transition metal content from one purification technology to another. Secondly, the metal content in SoG-Si materials is much higher than in mc-Si currently used in the production (the bottom graph in Fig. 1). SoG-Si available today contains practically every transition metal in concentrations between 3×10^{13} and 10^{16} cm^{-3} .

This raises the question if the purity of SoG-Si as it is available today is sufficient to make cells that can compete on the market with the cells made of electronic grade silicon. The question lies primarily in concentration of transition metals because their removal usually cannot be accomplished in the same processing step with removal of boron or phosphorus.

Metals are known to severely affect the minority carrier diffusion length and solar cell efficiency. Fig. 2 presents data for interstitial iron and FeB pairs from Ref. [39], data for Cu from Ref. [40], and our unpublished data for Ni. The shaded area on the plot indicates the range of minority carrier diffusion lengths typically found in mc-Si solar cells. One can see that the threshold concentration of interstitial iron acceptable for solar cells is around $2 \times 10^{12} \text{ cm}^{-3}$. Cu and Ni can be tolerated in concentrations up to 10^{14} – 10^{16} cm^{-3} . This conclusion is in agreement with experimental studies of efficiency of solar cells made of intentionally contaminated CZ ingots by Davis et al. [41]. They

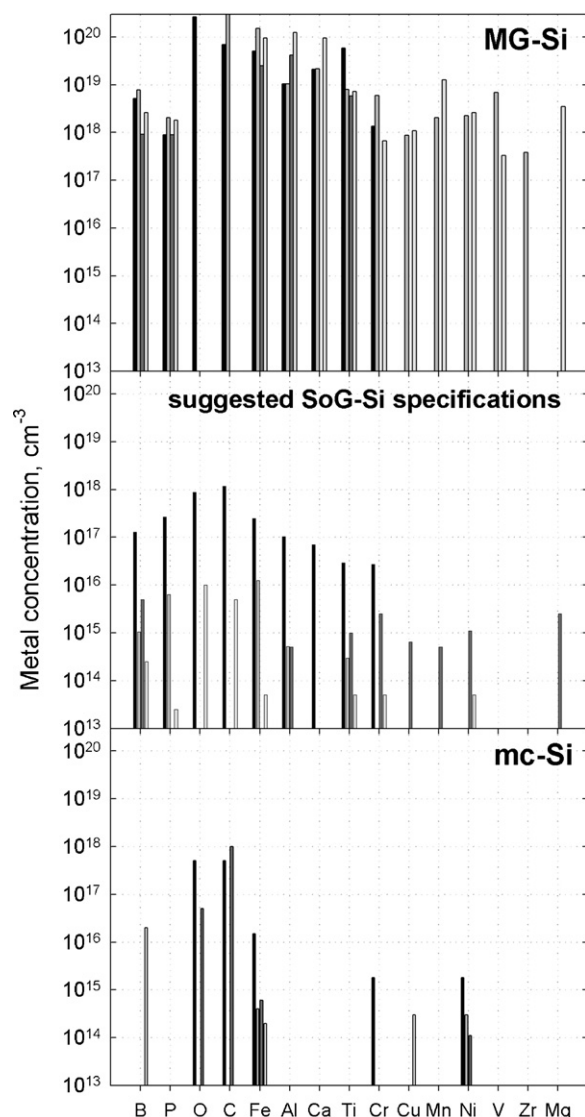


Fig. 1. Typical concentrations of impurities in metallurgical grade (the top graph), solar-grade (the middle graph), and multicrystalline silicon solar cells that are currently in production (the bottom graph). The data points are from Refs. [1,3,23,33–38]. Not all sources provide data for all elements. Lack of bars on the plots does not always mean that this element was not present above the detection limit but rather that it was not tested.

showed that Cu is the least detrimental metal impurity, while heavier metals such as Ti or W can degrade cell performance in concentrations as low as 10^{11} – 10^{12} cm⁻³.

Should one conclude that 10^{12} – 10^{13} cm⁻³ of transition metals is the limit which solar cells can tolerate? Surprisingly, neutron activation analyses [37,38,42] of several mc-Si materials used for commercial-scale manufacturing of solar cells revealed that these materials contain as much as 10^{15} cm⁻³ of iron, and 10^{12} – 10^{14} cm⁻³ of several other transition metals. If all these metals were homogeneously dissolved in the bulk in interstitial or substitutional state, the efficiency of solar cells would drop to unacceptably low levels. Our extensive X-ray microscopy studies using synchrotron radiation tools [43–46] revealed that, in fact, the majority of transition metals are found in metal precipitates or inclusions at grain boundaries or intragranular defects. In

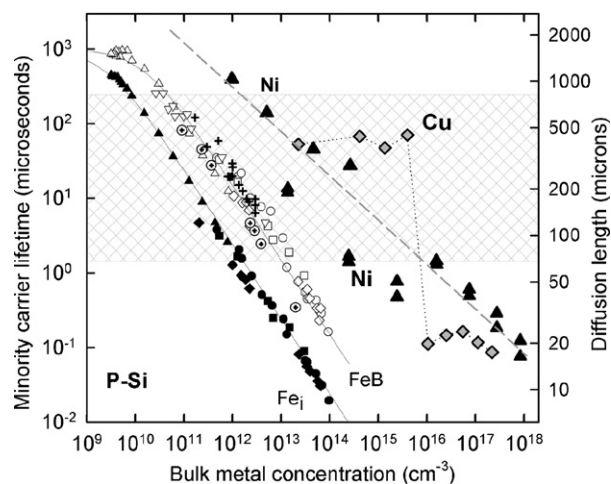


Fig. 2. Impact of iron, copper, and nickel on minority carrier diffusion length in single-crystalline silicon. The shaded area represents a typical range of minority carrier diffusion lengths in multicrystalline silicon solar cells.

this state, the recombination activity per metal atom is reduced as compared to interstitially dissolved metals, and the tolerance of solar cells to metal contamination increases.

It is even possible to intentionally manipulate the distribution of metals in mc-Si to change the minority carrier diffusion length. For example, rapid thermal annealing at high temperatures followed by a rapid cool can dissolve metal clusters and decrease the cell efficiency [47]. In contrast, a cooling regime which favors the formation of metal precipitates can substantially improve the minority carrier diffusion length [48]. We call this approach defect engineering of transition metals in silicon.

An example of defect engineering is shown in Fig. 3. For this experiment three mc-Si samples grown by the float zone technique were intentionally contaminated with Fe, Cu, and Ni at 1200 °C. The anneal was terminated by a silicone oil quench. The samples were etched to remove surface metal silicides. A

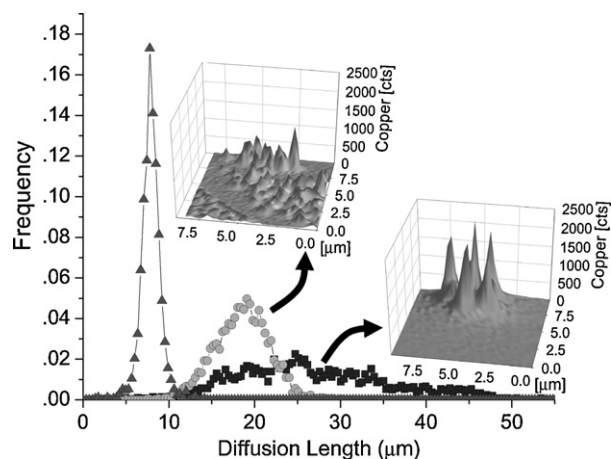


Fig. 3. Distribution of minority carrier diffusion lengths in multicrystalline silicon samples intentionally contaminated with Fe, Cu, and Ni and (triangles) quenched in silicone oil from 1200 °C; (circles) quenched in silicone oil, etched, and then reannealed at 655 °C and slowly cooled; and (squares) slowly cooled in the furnace from 1200 °C to room temperature. Inserts show μ-XRF maps of Cu-rich particles in slowly cooled and quenched and reannealed samples.

rapid quench is known to quench-in slowly diffusing metals in their interstitial state (such as iron, [39,49,50]) or form high density of small copper and nickel precipitates [51,52]. One of the three samples was used as a reference, the other two were reannealed. One was slowly cooled down from 1200 °C to room temperature, the other one was annealed for several hours at 655 °C and was also slowly cooled down to room temperature. Fig. 3 represents the distribution of minority carrier diffusion lengths and μ -XRF maps of metal clusters. It is important to remember that all three samples contain the same amount of transition metals. However, their minority carrier diffusion length differs by as much as a factor of four. A higher diffusion length correlates with metals found in a lower density of larger clusters.

We discussed above that SoG-Si which is currently produced in research and development programs contains high concentration of transition metals. One possible approach to use this material for solar cell production is to add an additional purification step to reduce the metal content by two to three orders of magnitude. This would increase the cost of the silicon feedstock. An alternative approach is to gain a deeper understanding of the interaction between metals and with structural defects in mc-Si in order to defect-engineer metals into their least recombination active state. This approach could involve specially designed heat treatments, optimization of growth conditions to favor the formation of preferred types and densities of grain boundaries or dislocations, shifting the balance between silicon interstitials or vacancies in the desired direction, utilization of defect reactions between metals with the formation of complexes and mixed silicides [53], etc. Additionally, one could use the improved understanding of defect reactions of metals to improve the efficiency of gettering and hydrogen passivation. A combination of impurity defect engineering with improved techniques for purification of MG-Si could lead to implementation of SoG-Si into mass-scale production in the near future.

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